

WHAT IS CLAIMED IS:

We claim:

1. A process to produce an ethylene polymer, the process comprising the steps of:

blending at least one chromium oxide catalyst carried on a first support, the chromium
oxide catalyst including compounds calcinable to chromium oxide at conditions used to
activate the chromium oxide catalyst, and at least one silyl chromium catalyst carried on a
second support to form a catalyst mixture, wherein the chromium oxide catalyst is present
in an amount from about 25 to about 50 weight percent based on the total weight of the
catalyst mixture and the silyl chromium catalyst is present in an amount of about 50 to
about 75 weight percent based on the total weight of the catalyst mixture;

introducing the catalyst mixture into a polymerization reactor, wherein at least one
monomer comprising ethylene is present in the reactor and the reactor is maintained at
polymerization conditions such that the at least one monomer will polymerize in the
presence of the catalyst mixture;

activating the chromium oxide catalyst either before or after the blending step but prior to
introducing the catalyst mixture into the reactor; and,

contacting the catalyst mixture and the at least one monomer in the reactor such that an
ethylene polymer is formed,

wherein the ethylene polymer is characterized, in comparison to an ethylene polymer
prepared under the same polymerization conditions in the presence of the chromium

oxide catalyst only, by an increase in environmental stress crack resistance (ESCR) at least about 400% and an increase in swell of no more than about 15%.

2. The process of Claim 1 wherein the first support and the second support have an average pore volume within 30% of each other.

5 3. The process of Claim 1 wherein the polymerization reactor is a gas phase reactor.

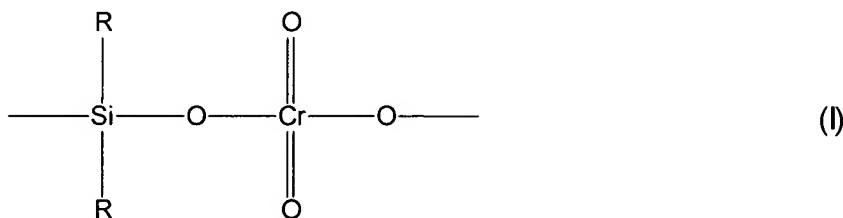
4. The process of Claim 1 wherein the monomer further comprises a C₃-C₂₀ α-olefin and/or a diene.

5. The process of Claim 4 wherein the α-olefin is 1-propene, 1-butene, 1-hexene, 1-octene or a combination thereof.

10 6. The process of Claim 1 wherein the chromium oxide catalyst is at least one of chromic acetyl acetone, chromic chloride, chromic nitrate, chromic acetate, chromic sulfate, ammonium chromate, or ammonium dichromate.

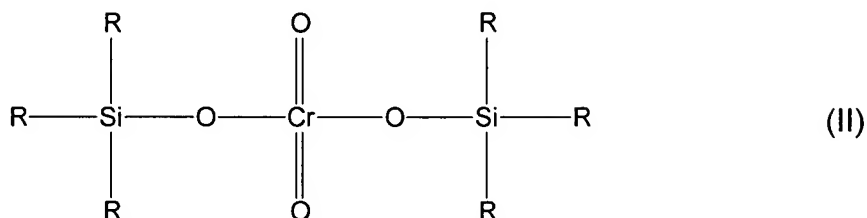
7. The process of Claim 1 wherein the silyl chromium catalyst is characterized by the presence of at least one group of Formula I:

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wherein R, each occurrence, is a hydrocarbyl group having from 1 to 14 carbon atoms.

8. The process of Claim 7 wherein silyl chromium catalyst is a bis-trihydrocarbylsilylchromate of Formula II:



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where R is defined as in Claim 7.

9. The process of Claim 1 wherein the silyl chromium catalyst is at least one of bis-trimethylsilylchromate, bis-triethylsilylchromate, bis-tributylsilylchromate, bis-triisopentylsilylchromate, bis-tri-2-ethylhexylsilylchromate, bis-tridecylsilylchromate, bis-tri(tetradecyl)silylchromate, bis-tribenzylsilylchromate, bis-triphenethylsilylchromate, bis-triphenylsilylchromate, bis-tritolylsilylchromate, bis-trixylylsilylchromate, bis-trinaphthylsilylchromate, bis-triethylphenylsilylchromate, bis-trimethylnaphthylsilylchromate, polydiphenylsilylchromate, or polydiethylsilylchromate.
10. The process of Claim 1 wherein the monomer further comprises at least one of propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene, and the dienes 5-ethylidene-2-norbornene and piperylene. Other useful monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutene, 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 4-vinylcyclohexene, and vinylcyclohexane, 2,5-norbornadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-butadiene, isoprene or naphthenics.
11. An ethylene polymer produced by the process of Claim 1.

12. A composition comprising the ethylene polymer of Claim 11.
13. An article comprising the ethylene polymer of Claim 1.
14. The article of Claim 13 which is a blow-molded article.
15. The article of Claim 14 which is a bottle.
- 5 16. The process of Claim 1 wherein the catalyst mixture is introduced into the reactor as a slurry in a viscous inert liquid.
17. A process to produce an ethylene polymer, the process comprising the steps of:

providing a polymerization reactor, wherein at least one monomer comprising ethylene is present in the reactor and the reactor is maintained at polymerization conditions;

10 continuously or intermittently introducing at least one activated chromium oxide catalyst carried on a first support into the reactor, the chromium oxide catalyst including compounds calcinable to chromium oxide at conditions used to activate the chromium oxide catalyst;

continuously or intermittently introducing at least one silyl chromium catalyst carried on

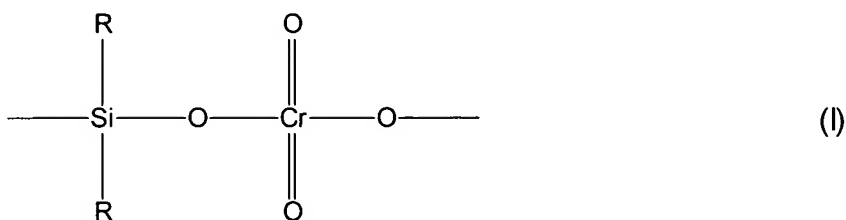
15 a second support into the reactor such that the chromium oxide catalyst is present in an amount from about 25 to about 50 weight percent and the silyl chromium catalyst is present in an amount of about 50 to about 75 weight percent based on the total weight of the catalysts present in the reactor; and,

contacting the chromium oxide catalyst, the silyl chromium catalyst and the monomer(s)

20 in the reactor such that an ethylene polymer is formed,

wherein the ethylene polymer is characterized, in comparison to an ethylene polymer prepared under the same polymerization conditions in the presence of the chromium oxide catalyst only, by an increase in environmental stress crack resistance (ESCR) at least about 400% and an increase in swell of no more than about 15%.

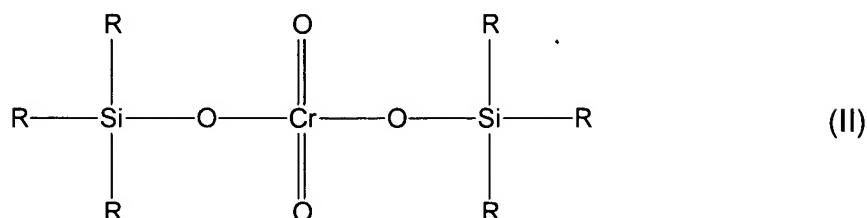
- 5 18. The process of Claim 17 wherein the first support and the second support have an average pore volume within 30% of each other.
19. The process of Claim 17 wherein the polymerization reactor is a gas phase reactor.
20. The process of Claim 17 wherein the monomer further comprises a C₃-C₂₀ α-olefin and/or a diene.
- 10 21. The process of Claim 20 wherein the α-olefin is 1-propene, 1-butene, 1-hexene, 1-octene or a combination thereof.
22. The process of Claim 17 wherein the chromium oxide catalyst is at least one of chromic acetyl acetone, chromic chloride, chromic nitrate, chromic acetate, chromic sulfate, ammonium chromate, or ammonium dichromate.
- 15 23. The process of Claim 17 wherein the silyl chromium catalyst is characterized by the presence of at least one group of Formula I:



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wherein R, each occurrence, is a hydrocarbyl group having from 1 to 14 carbon atoms.

24. The process of Claim 23 wherein silyl chromium catalyst is a bis-trihydrocarbylsilylchromate of Formula II:



where R is defined as in Claim 23.

25. The process of Claim 17 wherein the silyl chromium catalyst is at least one of bis-trimethylsilylchromate, bis-triethylsilylchromate, bis-tributylsilylchromate, bis-triisopentylsilylchromate, bis-tri-2-ethylhexylsilylchromate, bis-tridecylsilylchromate, bis-tri(tetradecyl)silylchromate, bis-tribenzylsilylchromate, bis-triphenethylsilylchromate, bis-triphenylsilylchromate, bis-tritolylsilylchromate, bis-trixylsilylchromate, bis-trinaphthylsilylchromate, bis-triethylphenylsilylchromate, bis-trimethylnaphthylsilylchromate, polydiphenylsilylchromate, or polydiethylsilylchromate.
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26. The process of Claim 17 wherein the monomer further comprises at least one of propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene, and the dienes 5-ethylidene-2-norbornene and piperylene. Other useful monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutene, 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 4-vinylcyclohexene, and vinylcyclohexane, 2,5-norbornadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-butadiene, isoprene or naphthenics.
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27. An ethylene polymer produced by the process of Claim 17.
28. A composition comprising the ethylene polymer of Claim 27.
29. An article comprising the ethylene polymer of Claim 17.
30. The article of Claim 29 which is a blow-molded article.
- 5 31. The article of Claim 30 which is a bottle.
32. The process of Claim 17 wherein at least one catalyst is introduced into the reactor as a slurry in a viscous inert liquid.